

## PATENT ABSTRACTS OF JAPAN

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(54) BATTERY SEPARATOR

(57)Abstract:

PROBLEM TO BE SOLVED: To improve alkali resistance, oxidation deterioration resistance and electrolyte holding property by forming the separator of a nonwoven fabric mainly composed of a specified polyamide.

SOLUTION: A dicarboxylic acid component containing 60 mole % or more of aromatic dicarboxylic acid is reacted with a diamine component containing 60 mole % or more of C6-12 fatty alkylenediamine to provide a polyamide having a ratio [CONH/CH<sub>2</sub>] in molecular chain of 1/2-1/8 and a critical viscosity (in concentrated sulfuric acid, 30° C) of 0.6-2.0dl/g. This polyamide is fused at a temperature of the melting point of polyamide or more and 360° C or less followed by fiber forming to provide a polyamide fiber. Fifty wt.% or more of this polyamide fiber is mixed with other fibers and fabricated to provide a battery separator formed on a nonwoven fabric.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The separator for cells which is a separator for cells formed from the nonwoven fabric which uses a polyamide as a principal component, and is characterized by this polyamide consisting of a dicarboxylic acid component more than whose 60 mol % of a dicarboxylic acid component is aromatic series dicarboxylic acid, and a diamine component more than whose 60 mol % of a diamine component is the aliphatic series alkylene diamine of carbon numbers 6-12.

[Claim 2] The separator for cells according to claim 1 characterized by aliphatic series alkylene diamine being 1 and 9-nonane diamine.

[Claim 3] The separator for cells according to claim 1 characterized by aliphatic series alkylene diamine consisting of 1 and 9-nonane diamine, and the 2-methyl -1 and 8-octane diamine.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] Especially this invention relates to the suitable separator for the cell which uses lye about the separator for cells.

[0002]

[Description of the Prior Art] As a separator for alkaline cells, the nonwoven fabric of a polyamide fiber, the nonwoven fabric of polyolefine fiber, etc. are known conventionally, and it is used for each cell using the property of each fiber. However, although its solution retention of the electrolytic solution is good since the nonwoven fabric which consists of aliphatic series polyamide fibers, such as a polyamide fiber especially nylon 6, and Nylon 66, is excellent in alkali resistance and excellent in the hydrophilic property, and it has the advantage also with a large discharge capacity, since it is inferior to hot anti-oxidation degradation nature, when it is used for an alkaline cell, there is a fault of oxidizing with the oxygen gas which occurs at the time of charge, and deteriorating. When it was used for the rechargeable battery with which charge and discharge are especially repeated at an elevated temperature, since it was inferior to the anti-oxidation degradation nature to the intense cell reaction in the electrolytic solution in an elevated temperature (60-80 degrees C), the problem which a degradation phenomenon produces and to say was at an early stage.

[0003] On the other hand, although it is excellent in alkali resistance and anti-oxidation degradation nature, since polyolefine fiber is inferior to a hydrophilic property, the solution retention of the electrolytic solution is low [ fiber ]. For this reason, by the closed mold cell with the bad permeability of the gas which occurs at the time of charge when the electric resistance in the inside of the electrolytic solution is high, there were problems, like there is a danger of internal pressure going up and exploding at the time of charge.

[0004] In order to improve the anti-oxidation degradation nature of the above-mentioned polyamide fiber, although mixing or compound-izing are proposed in a polyamide fiber and polyolefine fiber, since the mixing percentage (JP,55-25921,A, JP,55-66864,A, etc.) of the fiber which carries out oxidative degradation decreases as a whole, it stops at extent that degradation is mitigable, and it has not resulted in fundamental solution.

[0005] Moreover, in order to improve the solution retention of the electrolytic solution of polyolefine fiber, the approach of giving a hydrophilic property to polyolefine fiber is proposed. For example, many approaches, such as an approach of processing and sulfonating the separator of polyolefine fiber with an oleum or the Krol sulfuric acid, a method of processing and sulfonating in sulfur-trioxide gas, and the approach of carrying out the graft polymerization of an acrylic acid or the methacrylic acid by electron beam irradiation, are proposed. However, hydrophilization processing continues an expensive top at a long period of time, cannot maintain the hydrophilic property easily, and since it turns into processing under a severe condition, it has the trouble that fiber reinforcement falls.

[0006] The separator for cells using the nonwoven fabric which becomes the bottom of such a situation from aromatic polyamide or all aromatic polyamide is also proposed (JP,5-283054,A, JP,53-58636,A, JP,58-147956,A, etc.). Although this aromatic polyamide or all aromatic

polyamide are generally excellent in a hydrophilic property and being excellent in alkali resistance and anti-oxidation degradation nature, an adhesive property is low in itself, the nonwoven fabric with which thermal resistance becomes very high backlash only from this fiber has a problem in nonwoven fabric reinforcement, and its adhesive property with general thermoplastic binder fiber is also low, and a problem is in nonwoven fabric reinforcement too. In order to raise an adhesive property, there is also a method of performing resin adhesion, but when the nonwoven fabric pasted up by the approach of starting is used as a separator for cells, there is a problem to which adhesion resin is eluted in the electrolytic solution of a cell. Moreover, the separator which consists of MXD-6 fiber which consists of aromatic series diamine and aliphatic series dicarboxylic acid may be inferior to the anti-oxidation degradation nature in an elevated temperature, may oxidize with the oxygen gas which occurs at the time of charge, and may deteriorate.

[0007]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the separator for cells also with the anti-oxidation degradation nature which the nonwoven fabric which consists of polyolefine fiber has formed with the nonwoven fabric which uses a polyamide as a principal component, having a hydrophilic property, i.e., the solution retention of the electrolytic solution.

[0008]

[Means for Solving the Problem] This invention is the separator for cells formed from the nonwoven fabric which uses a polyamide as a principal component, and is a separator for cells characterized by this polyamide consisting of a dicarboxylic acid component more than whose 60 mol % of a dicarboxylic acid component is aromatic series dicarboxylic acid, and a diamine component more than whose 60 mol % of a diamine component is the aliphatic series alkylene diamine of carbon numbers 6-12.

[0009]

[Embodiment of the Invention] First, the polyamide which constitutes the separator for cells of this invention is explained. This polyamide consists of a dicarboxylic acid component and a diamine component, and it has the description for more than 60 mol % of a diamine component to be [ that more than 60 mol % of a dicarboxylic acid component is aromatic series dicarboxylic acid and ] the aliphatic series alkylene diamine of carbon numbers 6-12.

[0010] As aromatic series dicarboxylic acid, a terephthalic acid is desirable in respect of the alkali resistance of the separator for cells, and anti-oxidation degradation nature. Isophthalic acid, 2, 6-naphthalene dicarboxylic acid, 2, 7-naphthalene dicarboxylic acid, 1, 4-naphthalene dicarboxylic acid, 1, 4-phenylene dioxy diacetate, A 1,3-phenylenedioxy diacetate, diphenic acid, JI benzoic-acid, 4, and 4'-OKISHIJI benzoic acid, One or more kinds of aromatic series dicarboxylic acid, such as diphenylmethane -4, 4'-dicarboxylic acid, diphenylsulfone -4, and -dicarboxylic acid, and 4 '4, 4'-biphenyl dicarboxylic acid, can also be used, using it together. The content of this aromatic series dicarboxylic acid is more than 60 mol % of a dicarboxylic acid component, and it is desirable that it is more than 75 mol %. As dicarboxylic acid other than the above-mentioned aromatic series dicarboxylic acid, alicyclic dicarboxylic acid, such as aliphatic series dicarboxylic acid;1, such as malonic-acid, dimethyl malonic-acid, succinic-acid, 3, and 3-diethyl succinic-acid, glutaric-acid, 2, and 2-dimethyl glutaric-acid, adipic-acid, 2-methyl adipic-acid, trimethyl adipic-acid, pimelic-acid, azelaic-acid, sebacic-acid, and suberic acid, 3-cyclopentane dicarboxylic acid, 1, and 4-cyclohexane dicarboxylic acid, can be mentioned, and these acids can use not only one kind but two kinds or more. It is desirable that a dicarboxylic acid component is 100% aromatic series dicarboxylic acid especially in respect of the reinforcement of a nonwoven fabric, chemical resistance, anti-oxidation degradation nature, thermal resistance, etc. Multiple-valued carboxylic acids, such as trimellitic acid, trimesic acid, and pyromellitic acid, can also be made to contain within limits with easy fibrosis and nonwoven-fabric-izing furthermore.

[0011] A carbon number consists of aliphatic series alkylene diamines of 6-12 more than 60 mol % of a diamine component. Moreover, as this aliphatic series alkylene diamine 1, 6-hexanediamine, 1, 8-octane diamine, 1, 9-nonane diamine, 1, 10-Deccan diamine, 1, and 11-

undecane diamine, 1, 12-undecane diamine, The 2-methyl -1, 5-pentane diamine, the 3-methyl -1, 5-pentane diamine, 2, 2, 4-trimethyl -1, 6-hexanediamine, 2 and 4, 4-trimethyl -The aliphatic series diamine which has a straight chain or side chains, such as 1, 6-hexanediamine, the 2-methyl -1, 8-octane diamine, the 5-methyl -1, and 9-nonane diamine, can be mentioned. Concomitant use with 1, 9-nonane diamine, 1, and 9-nonane diamine, and the 2-methyl -1 and 8-octane diamine is desirable in respect of anti-oxidation degradation nature especially. Although the content of this aliphatic series alkylene diamine is more than 60 mol % of a diamine component, it is especially desirable more than 75 mol % and that it is more than 90 mol % in respect of electrolytic-solution solution retention.

[0012] As diamines other than above-mentioned aliphatic series alkylene diamine, ethylenediamine, Aliphatic series diamines, such as propylenediamine and 1,4-butanediamine; A cyclohexanediamine, Methylcyclohexane diamine, isophorone diamine, norbornane dimethyl diamine, Alicyclic diamines, such as tricyclodecane dimethyl diamine; P-phenylene diamine, m-phenylenediamine, xylylene diamine, xylene diamine, Aromatic series diamines, such as -diaminodiphenyl sulfone, and 4 and 4'-diamino diphenylmethane, 4, and 4 '4, 4'-diamino diphenyl ether, or such mixture can be mentioned, and these can use not only one kind but two kinds or more.

[0013] When using together 1 and 9-nonane diamine, and the 2-methyl -1 and 8-octane diamine as aliphatic series alkylene diamine, 60-100-mol% of a diamine component consists of 1 and 9-nonane diamine, and the 2-methyl -1 and 8-octane diamine, and, as for the mole ratio, it is especially desirable former:latter =30:70-99:1 and that it is former:latter =40:60-95:5.

[0014] Moreover, 1 / 2 - 1/8, and that it is especially 1 / 3 - 1/5 have [ the polyamide used for this invention ] the desirable ratio of [CONH/CH<sub>2</sub>] in the chain. The separator for cells excellent in alkali resistance, anti-oxidation degradation nature, and the solution retention of the electrolytic solution is obtained by using the polyamide of this range.

[0015] As for the limiting viscosity (value measured at 30 degrees C among concentrated sulfuric acid) of an above-mentioned polyamide, it is desirable that it is 0.6 - 2.0 dl/g, and 0.6 - 1.8 dl/g and its 0.7 - 1.6 dl/g are especially desirable. The polyamide of this limiting viscosity within the limits has fibrosis and a good melt viscosity property at the time of nonwoven-fabric-izing, and becomes the thing excellent in the reinforcement of the separator obtained further, alkali resistance, anti-oxidation degradation nature, etc.

[0016] As for a further above-mentioned polyamide, it is desirable that the closure of the 10% or more of the end group of the chain is carried out with end encapsulant, and its thing of an end further done for the closure of the 70% or more of an end is desirable 40% or more. By closing the end of a chain, it becomes the thing excellent in the reinforcement of the separator obtained, alkali resistance, anti-oxidation degradation nature, etc. Although there will be especially no limit if it is the compound of the monofunctional nature which has the amino group of a polyamide end or a carboxyl group, and reactivity as end encapsulant, monocarboxylic acid and monoamine are desirable from points, such as reactivity and the stability of a closure end. Monocarboxylic acid is desirable in respect of the ease of handling nature, reactivity, the stability of a closure end, a price, etc. As monocarboxylic acid, an acetic acid, a propionic acid, butanoic acid, a valeric acid, a caproic acid, a caprylic acid, a lauric acid, a tridecyl acid, a myristic acid, a palmitic acid, stearin acid, a benzoic acid, etc. can be mentioned. In addition, it can ask for the rate of the closure of an end from the integral value of the property signal corresponding to each end group by <sup>1</sup>H-NMR.

[0017] Especially the manufacture approach of the polyamide concerning this invention is not restricted, but can use the approach of the arbitration well-known as an approach which manufactures a crystalline polyamide. For example, it can manufacture by the approaches of using as a raw material the alkyl ester and diamine of the solution polymerization method which uses acid chloride and diamine as a raw material or interfacial polymerization, dicarboxylic acid, or dicarboxylic acid, such as a melting polymerization method and a solid-state-polymerization method.

[0018] If an example is given, after putting in block end encapsulant, a catalyst, a diamine component, and a dicarboxylic acid component, making them react and manufacturing nylon salt,

it can manufacture easily limiting viscosity's once considering a prepolymer of 0.15 – 0.30 dl/g in the temperature of 280 degrees C or less, and carrying out solid state polymerization further, or performing a polymerization using a melting extruder. When solid state polymerization performs the culmination of a polymerization, if it is the range whose polymerization temperature is 200–250 degrees C, a rate of polymerization is large, and since it excels in productivity and coloring and gelation can be controlled effectively, it is desirable [ it is desirable to carry out to the bottom of reduced pressure or inert gas circulation, and ]. When a melting extruder performs the culmination of a polymerization, since the polyamide which does not almost have decomposition of a polyamide as polymerization temperature is 370 degrees C or less, and does not have degradation is obtained, it is desirable.

[0019] As a polymerization catalyst, a phosphoric acid, phosphorous acid, hypophosphorous acid or those ammonium salt, those metal salts, and those ester can be mentioned, and sodium hypophosphite is desirable in respect of handling nature etc. in the ease of carrying out of acquisition especially. Moreover, stabilizers, such as a copper compound, a coloring agent, an ultraviolet ray absorbent, light stabilizer, an antioxidant, an antistatic agent, a flame retarder, a plasticizer, lubricant, a crystallization rate retarder, etc. can be added polycondensation reaction time or after that if needed. If alkali halide metallic compounds, such as halogenation copper compounds, such as organic system stabilizers, such as a hindered phenol, and copper iodide, and potassium iodide, are added especially as a thermostabilizer, since the melting stagnation stability in the case of fibrosis will improve, it is desirable.

[0020] Although melt spinning is carried out using a melting extruder and extension is usually given, as for the polyamide obtained as mentioned above, it is desirable to use a screw die pressing appearance machine. more than the melting point of a polyamide — the temperature of 360 degrees C or less — fusing — the melting residence time for less than 30 minutes — a mouthpiece — it can fibrose by spinning from a nozzle. If melting temperature and the residence time are within the limits of the above, the pyrolysis of the polyamide at the time of spinning can be controlled.

[0021] Although it does not limit especially, when using it as a material of the separator for cells, it is [ that what is necessary is just to set up the fineness of this polyamide fiber suitably by various applications ] desirable that it is 0.1–5 deniers because of deposit prevention of the metal which constitutes the solution retention, positive electrode, and negative electrode of the electrolytic solution, and the short circuit prevention by migration of an electrode active material. In addition, a circular cross section or a variant cross section is sufficient as a fiber cross section, and, in the case of a variant cross section, let the value converted into the circular cross section be a diameter of fiber. Moreover, although especially fiber length is not limited, either, it can set up suitably by the formation approach of a nonwoven fabric. For example, it is desirable that it is 1–30mm when forming a nonwoven fabric with a wet method, and when forming a nonwoven fabric with dry process, such as the card method and the air lei method, it is desirable that it is 10–70mm.

[0022] The separator for cells of this invention consists of a nonwoven fabric which formed the above-mentioned polyamide fiber as a subject. As for a polyamide fiber, it is desirable that it is 50 % of the weight or more among a nonwoven fabric, and it is desirable that it is especially 70 % of the weight or more so that it may excel in the solution retention of the electrolytic solution.

[0023] In addition, the cellulosic fiber which mercerized the fiber; natural cellulose fiber of the compound gestalt which consists of polyolefine system resin independent, such as general-purpose aliphatic series polyamide; ethylene-vinyl alcohol system copolymers, such as nylon 6 and Nylon 66, polypropylene, polyethylene, polybutene, the poly methyl pentene, ethylene propylene rubber, and an ethylene-butene copolymer, or two kinds as fiber other than an above-mentioned polyamide fiber; the pulp by which marcerization was carried out can be mentioned. Moreover, the gestalt stability of a nonwoven fabric can also be raised by using fiber with the melting point lower than an above-mentioned polyamide fiber, well-known thermofusion nature binder fiber, a sizing agent, etc.

[0024] The nonwoven fabric concerning this invention can be obtained by the manufacture approach of arbitration. Fiber Webb (thing before interlacement of a nonwoven fabric or

association) can be formed, and it can manufacture with a general means to nonwoven-fabric-ize, by making the fiber in fiber Webb paste up or interlace. The obtained nonwoven fabric may be used as it is, and may be used as a layered product of two or more sheets. If there are wet methods, such as dry process, such as the card method and the air lei method, and a paper-making method, a span bond method, the melt blowing method, etc., for example, and fiber Webb obtained by the wet method or the melt blowing method also in these is precise, and it has a uniform surface state as fiber Webb's formation approach and is used as a separator for cells, since a deposit of a metal and migration of an electrode active material can be prevented, it is suitable fiber Webb's formation approach. moreover, it can also be used combining fiber Webb formed by the approach of each above, carrying out a laminating.

[0025] An all directions method is explained concretely. Although formation of fiber Webb by dry process can manufacture fiber Webb using a roller card, Randa Muka-DO, a webber, etc. and this UEBBU is classified by parallel Webb, a clo sault ebb, a coulisse clo sault ebb, semi random Webb, and random Webb with the directivity of fiber, since the difference of a longitudinal direction and the direction of width on the strength becomes small, Webb of the configuration where the orientation approach of fiber crossed is suitable.

[0026] the approach of, for example, making fiber Webb interlacing according to an operation of a stream, a needle, etc. as an approach of forming a nonwoven fabric from such fiber Webb, the approach of making it paste with a binder, and sewing thread — a web — length — there is the approach of suturing reticulated etc., and these approaches are independent or can be combined.

[0027] Although formation of fiber Webb by the wet method has a common paper-making method, the approach of starting has a quick production rate compared with other approaches, and has the advantage which can mix the fiber from which the diameter of fiber differs with the same equipment, and the fiber of two or more classes at a rate of arbitration. That is, the gestalt of fiber also has the wide width of face of the shape of the shape of a staple, and pulp, etc. and selection, the application range is very wide and good Webb of formation who went that the diameter of use fiber was also usable to fiber thick from super-thin fiber is obtained. This approach is the approach of cutting first the fiber obtained by carrying out melt spinning, distributing underwater, considering as a uniform paper-making slurry also with that of churning gently, and carrying out paper making of this slurry for paper making using the paper machine which has at least one of the wires, such as a round mesh, a long network, and an inclination type. Moreover, a stream may be applied to independence or the sheet which carried out the laminating, and it may be made to interlace the wet paper web obtained by doing in this way, or the paper after desiccation. After beating processing is performed by the beater or the refiner, you may succeed in the cut fiber with a paper-making slurry, and it may add a \*\* agent, a dispersant, etc. in the case of paper making.

[0028] When forming the nonwoven fabric of 100% of polyamide fibers which contains neither adhesives nor other fiber substantially, the melt blowing method which blows off an elevated-temperature air current from a perimeter, \*\*-izes fiber, carrying out melt spinning, and accumulates this on an uptake side is suitable. Moreover, the span bond method which the \*\*-ized-extension-Webb formation process linked directly can also be used cooling the spun fiber, the extension approach is good also by the roller also in an air jet, and filamentation can be performed by the frictional electrification method, the compulsive charging method, the collision diffusion method, an air-current diffusion method, etc.

[0029] As for the front face of the nonwoven fabric formed by such approach, it is desirable to perform heat calendering for the manifestation of the improvement of surface smooth nature, thickness adjustment of a nonwoven fabric, reinforcement, and densification etc.

[0030] It is also possible to form a nonwoven fabric by Bath with the split film method or the foaming film method and the fiber method besides having mentioned above.

[0031] The separator for cells of this invention can be used as primary or a separator for rechargeable batteries. An open sand mold or closed mold is sufficient as this cell, and a cylindrical shape, a flat form, and a square shape are sufficient also as a configuration. It can more specifically be suitably used as a separator of rechargeable batteries, such as primary cells,



such as an alkaline manganese dioxide cell, a mercury cell, a silver-zinc cell, and an air cell, a nickel-cadmium battery, a silver-zinc cell, a silver-cadmium cell, a nickel-zinc cell, a nickel hydride battery, and a rechargeable lithium-ion battery. In addition, although this invention is a separator for cells, the nonwoven fabric concerning this invention is useful also as an air filter and a liquid filter.

[0032]

[Example] Hereafter, although this invention is explained in full detail according to an example, this invention is not limited at all by these examples. In addition, each measured value in an example is a value measured by the following approaches.

(1) The basis weight of a nonwoven fabric (g/m<sup>2</sup>)

JIS P According to 8124, the nonwoven fabric was cut out on 10cm square, the weight W was measured with the electronic balance (the Metra Corp-company make, AE160 mold), and it computed by  $W/0.01$ .

(2) Powerful and breaking length of a nonwoven fabric (km)

JIS P the test piece which cut out the nonwoven fabric to 15mmx250mm according to 8113 — using — being powerful (kg / 15mm) — it measured and breaking length was computed.

(3) Air permeability (cc/m<sup>2</sup> / sec)

JIS L According to 1096, the nonwoven fabric was cut out on 20cm square, it considered as the test piece, and the air content which passes a test piece using the Flagyl mold testing machine was calculated.

[0033] (4) Alkali-proof JIS P According to 8113, immersion processing of the test piece of a nonwoven fabric was carried out for 60 hours into 70 degrees C and 10% of sodium-hydroxide water solution. The strength (kg / 15mm) of the test piece before and behind processing was measured, and it expressed with the retention on the strength.

(5) Anti-oxidation degradation nature JIS P It applies to 8113 correspondingly and is 5%KMnO<sub>4</sub> about the test piece of a nonwoven fabric. Immersion processing was carried out 30% for 1 hour at the mixed solution (the former/latter = 250/50 cc, 50 degrees C) of a potassium hydroxide. The strength (kg / 15mm) of the test piece before and behind processing was measured, and it expressed with the retention on the strength.

(6) Immersion processing of the test piece which cut the electrolytic-solution solution retention nonwoven fabric on 5cm square was carried out for 30 minutes at 20 degrees C and 30% of potassium hydroxide solution, and the liquid end by natural fall was performed in 30-second interspace mind. It is the weight of the test piece after W<sub>0</sub> and processing about the weight of the test piece before processing W<sub>1</sub> It carried out and the weight ratio ( $W_1 / W_0$ ) was computed as comprehensive liquid adsorption (g/g).

(7) Acid resistance JIS P According to 8113, immersion processing of the test piece of a nonwoven fabric was carried out for 100 hours into 70 degrees C and 10% of sulfuric-acid water solution. The strength (kg / 15mm) of the test piece before and behind processing was measured, and it expressed with the retention on the strength.

[0034] The terephthalic acid, 1, 9-nonane diamine, the 2-methyl -1, 8-octane diamine, the benzoic acid, the sodium hypophosphite-hydrate (it is 0.1 % of the weight to a raw material), and 2.2l. of distilled water of the amount shown in one to example of reference 7 table 1 were added to the autoclave of 20l. of content volume, and the nitrogen purge was performed. Subsequently, it agitated for 30 minutes at 100 degrees C, and the temperature up of the inside \*\* was carried out to 210 degrees C over 2 hours. At this time, the pressure up of the autoclave was carried out to 22kg/cm<sup>2</sup>. After continuing a reaction then for 1 hour, a temperature up is carried out to 230 degrees C, and it keeps at 230 degrees C after that for 2 hours, a steam is extracted gradually, and it is a pressure 22kg/cm<sup>2</sup> The reaction was continued holding. next, 30 minutes — applying — a pressure — 10kg/cm<sup>2</sup> up to — the prepolymer was obtained for the reaction continuously [ it lowered and / for further 1 hour ]. Under 100 degrees C and reduced pressure, it dried for 12 hours and this prepolymer was ground to the magnitude of 2mm or less. The polymer was obtained by carrying out solid state polymerization of the grinding object under 230 degrees C and 0.1mmHg for 10 hours. The limiting viscosity of the obtained polymer is shown in Table 1.



[0035]

[Table 1]

		参考例1 PA9T	参考例2 PA9MT	参考例3 PA9MT	参考例4 PA9MT	参考例5 PA9MT	参考例6 PA9T	参考例7 PA9MT
組成	TA (モル)	19.4	19.7	19.5	19.5	19.6	20.0	20.2
	NMDA (モル)	20.0	17.0	14.0	10.0	10.0	20.0	17.0
	MODA (モル)	—	3.0	6.0	10.0	10.0	—	3.0
	安息香酸 (モル)	1.2	0.6	1.0	1.0	0.8	0.4	0.3
	NaH <sub>2</sub> PO <sub>2</sub> H <sub>2</sub> O (モル)	0.06	0.06	0.06	0.06	0.06	0.06	0.06
極限粘度		0.8	1.3	0.8	0.9	0.9	1.1	1.0
CONH/CH <sub>2</sub>		1/4.5	1/4.3	1/4.1	1/3.9	1/3.9	1/4.5	1/4.3

TA : テレフタル酸

NMDA : 1, 9-ノナンジアミン

MODA : 2-メチル-1, 8-オクタンジアミン

[0036] Melting extrusion of the polymer obtained in an example 1 – the examples 1-7 of 7 reference was carried out using the extruder, each rate was adjusted so that the ratio (draft) of discharge, a regurgitation rate, and a winding rate might become the range of 10-50 from the round hole nozzle of 0.2mm phix200 holes, and it rolled round in the 500-2000m range for /in winding rate. Subsequently, 85 degrees C and two baths performed extension / contraction processing using the water bath it is [ water bath ] 95 degrees C, and one bath obtained the tow of about 600 deniers / 200 filament. Draw magnification was performed by 0.8 times of the maximum draw magnification. 10% of the weight, it mixed 30% of the weight, and the synthetic pulp SWP (Mitsui petrochemical company make: E-400) which consists what cut the obtained tow in die length of 5mm of polyethylene 60% of the weight was used as the raw material for the thermofusion nature binder fiber (Daiwabo [ Co., Ltd. ] make: NBF-1) of polyethylene/polypropylene. Paper making of this raw material is carried out with a cylinder machine, and they are basis-weight about 70 g/m<sup>2</sup>. The nonwoven fabric was created. The heat press of this nonwoven fabric was carried out at 120 degrees C, and the separator for cells was obtained. These separators (nonwoven fabric) are evaluated and a result is shown in Table 2.

[0037] As example 8 polymer, it is a 2159.8 g (13. zero mol) terephthalic acid, The polymerization of the polymer (PA66IT is called) was carried out like the example 1 of reference except having used 830.2g (5.0 mols) of isophthalic acid, adipic acids 292.3g (2.0 mols) and 1, 2324.2 g (20. zero mol) 6-hexanediamine, a 24.43 g (0.2 mols) benzoic acid, 6.6g of sodium hypophosphite-hydrates, and 2.2l. of distilled water (limiting viscosity = 0.8, CONH/CH<sub>2</sub> = 1/3.6). The separator was created by the paper-making method like the example 1 using obtained PA66IT. This separator is evaluated and a result is shown in Table 2.

[0038] As example 9 polymer, it is a 1960.3 g (11. eight mols) terephthalic acid, isophthalic acid 1302. — the polymerization of the polymer (PA10IT is called) was carried out like the example 1 of reference except having used 5g (7.8 mols), 1, 3446.2 g (20. zero mol) 10-Deccan diamine, a 97.7 g (0.8 mols) benzoic acid, 6.2g of sodium hypophosphite-hydrates, and 6l. of distilled water (limiting viscosity = 0.8, CONH/CH<sub>2</sub> = 1/5). The separator was created by the paper-making method like the example 1 using obtained PA10IT. This separator is evaluated and a result is shown in Table 2.

[0039] The separator for cells was created by the paper-making method like the example 1 except having used the nylon 6 (Ube Industries [, Ltd. ] make: UBE nylon 6) to which ring opening polymerization of the example of comparison 1 caprolactam was carried out. This separator is evaluated and a result is shown in Table 2. Although it excelled in alkali resistance and electrolytic-solution solution retention so that clearly from the result of Table 2, anti-oxidation degradation nature was low.

[0040] The separator for cells was created by the paper-making method like the example 1 except having used Nylon 66 (Ube Industries [, Ltd. ] make: UBE Nylon 66) which consists of

example of comparison 2 diamethylenediamine (aliphatic series diamine), and an adipic acid (aliphatic series dicarboxylic acid). This separator is evaluated and a result is shown in Table 2. Although it excelled in alkali resistance and electrolytic-solution solution retention so that clearly from the result of Table 2, anti-oxidation degradation nature was low.

[0041] The separator for cells was created by the paper-making method like the example 1 except having used the polyamide (Mitsubishi Gas Chemical [ Co., Inc. ] make: MX nylon 6007) which consists of example of comparison 3 meta-xylylene diamine (aromatic series diamine), and an adipic acid (aliphatic series dicarboxylic acid). This separator is evaluated and a result is shown in Table 2. Although it was thought because crystallinity is low that amide association was structurally weak since the polyamide consisted of aliphatic series JIKARUBON, in the anti-oxidation deterioration test, oxidation degradation was remarkably carried out in test fluid, and the configuration of a test piece did not remain.

[0042] 40% of the weight, it mixed 30% of the weight, the synthetic pulp SWP (Mitsui petrochemical company make: E-400) which consists of polyethylene the polyamide fiber (what was cut) by which spinning was carried out in the example of comparison 4 example 4 30% of the weight was used as the raw material for the thermofusion nature binder fiber (Daiwabo [ Co., Ltd. ] make: NBF) of polyethylene/polypropylene, and the battery separator was created by the paper-making method. This separator is evaluated and a result is shown in Table 2. Since there were few amounts of the polyamide fiber in a separator, electrolytic-solution solution retention was low.

[0043] The separator for cells was created by the paper-making method using example of comparison 5 polypropylene (Ube Industries [ , Ltd. ] make: ZS1330). This separator is evaluated and a result is shown in Table 2. Although excelled in alkali resistance and anti-oxidation degradation nature, electrolytic-solution solution retention was low.

[0044]

[Table 2]

	材料種類	試験温度 ℃	評価項目		評価結果		結果		
			坪量 g/m <sup>2</sup>	強度 kg/15mm	裂断長 Km	透気度 cc/m <sup>2</sup> /sec	耐水性 %	耐酸液性 %	保液性 g/g
実施例 1	PA9T	340	69.9	0.61	0.58	18.4	99	97	2.61
" 2	PA9MT	330	70.0	0.71	0.68	16.4	95	93	2.76
" 3	PA9MT	330	72.3	0.70	0.65	17.1	94	94	2.59
" 4	PA9MT	310	71.1	0.80	0.75	17.8	98	98	2.64
" 5	PA9MT	310	70.8	0.68	0.64	18.1	97	94	2.80
" 6	PA9T	340	70.6	0.65	0.61	16.8	98	96	2.72
" 7	PA9MT	330	71.2	0.60	0.56	17.6	97	95	2.61
" 8	PA66IT	335	69.8	0.42	0.40	16.9	98	88	2.55
" 9	PA10IT	310	70.3	0.55	0.52	16.5	96	89	2.54
比較例 1	PA6	270	72.2	0.56	0.52	20.6	95	20	2.93
" 2	PA66	290	71.9	0.71	0.66	15.6	97	16	2.81
" 3	MXD	280	70.6	0.40	0.38	16.2	98	18	2.70
" 4	PA9MT	310	72.1	0.49	0.45	13.4	98	95	2.23
" 5	PP	220	71.1	0.71	0.67	10.1	100	100	2.09

[0045] The polymer obtained in an example 10 - the examples 1 and 4 of 11 reference was nonwoven-fabric-ized by the melt blowing method using the rectangle nozzle of 0.45mm phix300 holes. Manufacture conditions are shown in Table 3. Distance between a spinning nozzle and a collector was performed by 30-300mm. The embossing calender-equipment set as 15% of sticking-by-pressure aspect products at the temperature which showed each nonwoven fabric in Table 3 performed embossing processing, and the separator was obtained. Each separator is evaluated and a result is shown in Table 3.

[0046] Nonwoven fabric-ization was performed by the melt blowing method like the example 9 using six to example of comparison 8 nylon 6, MX nylon, and polypropylene. Subsequently, embossing processing was performed and the separator was obtained. Each separator is

evaluated and a result is shown in Table 3.

[0047]

[Table 3]

ポリマーの種類		実施例10	実施例11	比較例6	比較例7	比較例8
		PA9T	PA9MT	PA6	MXD	PP
製 造 条 件	ノズル温度(℃)	345	330	310	290	290
	空気温度 (℃)	350	350	340	320	320
	空気圧力	2.8	2.7	2.5	2.3	2.1
	ヒーター 温度(℃)	200	180	150	150	130
評 価	坪量 (g/m <sup>2</sup> )	73	74	69	72	71
	強力 (kg/15mm)	1.5	1.8	0.8	0.7	1.1
	裂断長 (mm)	1.37	1.62	0.78	0.65	1.03
	透気度(cc/m <sup>2</sup> /sec)	33.6	35.4	30.8	34.0	37.1
	耐アルカリ性(%)	98	99	95	98	100
	耐酸化劣化性(%)	99	98	0	0	100
低	保液性(g/g) 総合	2.78	2.84	3.32	2.80	2.19
	耐酸性 (%)	99	98	0	0	100

[0048]

[Effect of the Invention] Alkali resistance, anti-oxidation degradation nature, electrolytic-solution solution retention, etc. have the engine performance effective in a separator, and the separator for cells of this invention can use them for a long period of time [ various cell applications ].

[Translation done.]

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**TECHNICAL FIELD**

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[The technical field to which invention belongs] Especially this invention relates to the suitable separator for the cell which uses lye about the separator for cells.

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PRIOR ART

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[Description of the Prior Art] As a separator for alkaline cells, the nonwoven fabric of a polyamide fiber, the nonwoven fabric of polyolefine fiber, etc. are known conventionally, and it is used for each cell using the property of each fiber. However, although its solution retention of the electrolytic solution is good since the nonwoven fabric which consists of aliphatic series polyamide fibers, such as a polyamide fiber especially nylon 6, and Nylon 66, is excellent in alkali resistance and excellent in the hydrophilic property, and it has the advantage also with a large discharge capacity, since it is inferior to hot anti-oxidation degradation nature, when it is used for an alkaline cell, there is a fault of oxidizing with the oxygen gas which occurs at the time of charge, and deteriorating. When it was used for the rechargeable battery with which charge and discharge are especially repeated at an elevated temperature, since it was inferior to the anti-oxidation degradation nature to the intense cell reaction in the electrolytic solution in an elevated temperature (60-80 degrees C), the problem which a degradation phenomenon produces and to say was at an early stage.

[0003] On the other hand, although it is excellent in alkali resistance and anti-oxidation degradation nature, since polyolefine fiber is inferior to a hydrophilic property, the solution retention of the electrolytic solution is low [ fiber ]. For this reason, by the closed mold cell with the bad permeability of the gas which occurs at the time of charge when the electric resistance in the inside of the electrolytic solution is high, there were problems, like there is a danger of internal pressure going up and exploding at the time of charge.

[0004] In order to improve the anti-oxidation degradation nature of the above-mentioned polyamide fiber, although mixing or compound-izing are proposed in a polyamide fiber and polyolefine fiber, since the mixing percentage (JP,55-25921,A, JP,55-66864,A, etc.) of the fiber which carries out oxidative degradation decreases as a whole, it stops at extent that degradation is mitigable, and it has not resulted in fundamental solution.

[0005] Moreover, in order to improve the solution retention of the electrolytic solution of polyolefine fiber, the approach of giving a hydrophilic property to polyolefine fiber is proposed. For example, many approaches, such as an approach of processing and sulfonating the separator of polyolefine fiber with an oleum or the Krol sulfuric acid, a method of processing and sulfonating in sulfur-trioxide gas, and the approach of carrying out the graft polymerization of an acrylic acid or the methacrylic acid by electron beam irradiation, are proposed. However, hydrophilization processing continues an expensive top at a long period of time, cannot maintain the hydrophilic property easily, and since it turns into processing under a severe condition, it has the trouble that fiber reinforcement falls.

[0006] The separator for cells using the nonwoven fabric which becomes the bottom of such a situation from aromatic polyamide or all aromatic polyamide is also proposed (JP,5-283054,A, JP,53-58636,A, JP,58-147956,A, etc.). Although this aromatic polyamide or all aromatic polyamide are generally excellent in a hydrophilic property and being excelled in alkali resistance and anti-oxidation degradation nature, an adhesive property is low in itself, the nonwoven fabric with which thermal resistance becomes eye high backlash only from this fiber has a problem in nonwoven fabric reinforcement, and its adhesive property with general thermoplastic binder fiber is also low, and a problem is in nonwoven fabric reinforcement too. In order to raise an adhesive

property, there is also a method of performing resin adhesion, but on the nonwoven fabric pasted up by the approach of starting is used as a separator for cells, there is a problem to which adhesion resin is eluted in the electrolytic solution of a cell. Moreover, the separator which consists of MXD-6 fiber which consists of aromatic series diamine and aliphatic series dicarboxylic acid may be inferior to the anti-oxidation degradation nature in an elevated temperature, may oxidize with the oxygen gas which occurs at the time of charge, and may deteriorate.

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**EFFECT OF THE INVENTION**

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[Effect of the Invention] Alkali resistance, anti-oxidation degradation nature, electrolytic-solution solution retention, etc. have the engine performance effective in a separator, and the separator for cells of this invention can use them for a long period of time [ various cell applications ].

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] The purpose of this invention is to offer the separator for cells also with the anti-oxidation degradation nature which the nonwoven fabric which consists of polyolefine fiber has formed with the nonwoven fabric which uses a polyamide as a principal component, having a hydrophilic property, i.e., the solution retention of the electrolytic solution.

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MEANS

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[Means for Solving the Problem] This invention is the separator for cells formed from the nonwoven fabric which uses a polyamide as a principal component, and is a separator for cells characterized by this polyamide consisting of a dicarboxylic acid component more than whose 60 mol % of a dicarboxylic acid component is aromatic series dicarboxylic acid, and a diamine component more than whose 60 mol % of a diamine component is the aliphatic series alkylene diamine of carbon numbers 6-12.

[0009]

[Embodiment of the Invention] First, the polyamide which constitutes the separator for cells of this invention is explained. This polyamide consists of a dicarboxylic acid component and a diamine component, and it has the description for more than 60 mol % of a diamine component to be [ that more than 60 mol % of a dicarboxylic acid component is aromatic series dicarboxylic acid and ] the aliphatic series alkylene diamine of carbon numbers 6-12.

[0010] As aromatic series dicarboxylic acid, a terephthalic acid is desirable in respect of the alkali resistance of the separator for cells, and anti-oxidation degradation nature. Isophthalic acid, 2, 6-naphthalene dicarboxylic acid, 2, 7-naphthalene dicarboxylic acid, 1, 4-naphthalene dicarboxylic acid, 1, 4-phenylene dioxy diacetate, A 1,3-phenylenedioxy diacetate, diphenic acid, JI benzoic-acid, 4, and 4'-OKISHIJI benzoic acid, One or more kinds of aromatic series dicarboxylic acid, such as diphenylmethane -4, 4'-dicarboxylic acid, diphenylsulfone -4, and -dicarboxylic acid, and 4 '4, 4'-biphenyl dicarboxylic acid, can also be used, using it together. The content of this aromatic series dicarboxylic acid is more than 60 mol % of a dicarboxylic acid component, and it is desirable that it is more than 75 mol %. As dicarboxylic acid other than the above-mentioned aromatic series dicarboxylic acid, alicyclic dicarboxylic acid, such as aliphatic series dicarboxylic acid;1, such as malonic-acid, dimethyl malonic-acid, succinic-acid, 3, and 3-diethyl succinic-acid, glutaric-acid, 2, and 2-dimethyl glutaric-acid, adipic-acid, 2-methyl adipic-acid, trimethyl adipic-acid, pimelic-acid, azelaic-acid, sebacic-acid, and suberic acid, 3-cyclopentane dicarboxylic acid, 1, and 4-cyclohexane dicarboxylic acid, can be mentioned, and these acids can use not only one kind but two kinds or more. It is desirable that a dicarboxylic acid component is 100% aromatic series dicarboxylic acid especially in respect of the reinforcement of a nonwoven fabric, chemical resistance, anti-oxidation degradation nature, thermal resistance, etc. Multiple-valued carboxylic acids, such as trimellitic acid, trimesic acid, and pyromellitic acid, can also be made to contain within limits with easy fibrosis and nonwoven-fabric-izing furthermore.

[0011] A carbon number consists of aliphatic series alkylene diamines of 6-12 more than 60 mol % of a diamine component. Moreover, as this aliphatic series alkylene diamine 1, 6-hexanediamine, 1, 8-octane diamine, 1, 9-nonane diamine, 1, 10-Decan diamine, 1, and 11-undecane diamine, 1, 12-dodecane diamine, The 2-methyl -1, 5-pentane diamine, the 3-methyl -1, 5-pentane diamine, 2, 2, 4-trimethyl -1, 6-hexanediamine, 2 and 4, 4-trimethyl -The aliphatic series diamine which has a straight chain or side chains, such as 1, 6-hexanediamine, the 2-methyl -1, 8-octane diamine, the 5-methyl -1, and 9-nonane diamine, can be mentioned. Concomitant use with 1, 9-nonane diamine, 1, and 9-nonane diamine, and the 2-methyl -1 and 8-octane diamine is desirable in respect of anti-oxidation degradation nature especially. Although

the content of this aliphatic series alkylene diamine is more than 60 mol % of a diamine component, it is especially desirable more than 75 mol % and that it is more than 90 mol % in respect of electrolytic-solution solution retention.

[0012] As diamines other than above-mentioned aliphatic series alkylene diamine, ethylenediamine, Aliphatic series diamines, such as propylenediamine and 1,4-butanediamine; A cyclohexanediamine, Methylcyclohexane diamine, isophorone diamine, norbornane dimethyl diamine, Alicyclic diamines, such as tricyclodecane dimethyl diamine; P-phenylene diamine, m-phenylenediamine, xylylene diamine, xylene diamine, Aromatic series diamines, such as -diaminodiphenyl sulfone, and 4 and 4'-diamino diphenylmethane, 4, and 4',4'-diamino diphenyl ether, or such mixture can be mentioned, and these can use not only one kind but two kinds or more.

[0013] When using together 1 and 9-nonane diamine, and the 2-methyl -1 and 8-octane diamine as aliphatic series alkylene diamine, 60-100-mol% of a diamine component consists of 1 and 9-nonane diamine, and the 2-methyl -1 and 8-octane diamine, and, as for the mole ratio, it is especially desirable former:latter =30:70-99:1 and that it is former:latter =40:60-95:5.

[0014] Moreover,  $1/2 - 1/8$ , and that it is especially  $1/3 - 1/5$  have [ the polyamide used for this invention ] the desirable ratio of [CONH/CH<sub>2</sub>] in the chain. The separator for cells excellent in alkali resistance, anti-oxidation degradation nature, and the solution retention of the electrolytic solution is obtained by using the polyamide of this range.

[0015] As for the limiting viscosity (value measured at 30 degrees C among concentrated sulfuric acid) of an above-mentioned polyamide, it is desirable that it is 0.6 - 2.0 dl/g, and 0.6 - 1.8 dl/g and its 0.7 - 1.6 dl/g are especially desirable. The polyamide of this limiting viscosity within the limits has fibrosis and a good melt viscosity property at the time of nonwoven-fabric-izing, and becomes the thing excellent in the reinforcement of the separator obtained further, alkali resistance, anti-oxidation degradation nature, etc.

[0016] As for a further above-mentioned polyamide, it is desirable that the closure of the 10% or more of the end group of the chain is carried out with end encapsulant, and its thing of an end further done for the closure of the 70% or more of an end is desirable 40% or more. By closing the end of a chain, it becomes the thing excellent in the reinforcement of the separator obtained, alkali resistance, anti-oxidation degradation nature, etc. Although there will be especially no limit if it is the compound of the monofunctional nature which has the amino group of a polyamide end or a carboxyl group, and reactivity as end encapsulant, monocarboxylic acid and monoamine are desirable from points, such as reactivity and the stability of a closure end. Monocarboxylic acid is desirable in respect of the ease of handling nature, reactivity, the stability of a closure end, a price, etc. As monocarboxylic acid, an acetic acid, a propionic acid, butanoic acid, a valeric acid, a caproic acid, a caprylic acid, a lauric acid, a tridecyl acid, a myristic acid, a palmitic acid, stearin acid, a benzoic acid, etc. can be mentioned. In addition, it can ask for the rate of the closure of an end from the integral value of the property signal corresponding to each end group by <sup>1</sup>H-NMR.

[0017] Especially the manufacture approach of the polyamide concerning this invention is not restricted, but can use the approach of the arbitration well-known as an approach which manufactures a crystalline polyamide. For example, it can manufacture by the approaches of using as a raw material the alkyl ester and diamine of the solution polymerization method which uses acid chloride and diamine as a raw material or interfacial polymerization, dicarboxylic acid, or dicarboxylic acid, such as a melting polymerization method and a solid-state-polymerization method.

[0018] If an example is given, after putting in block end encapsulant, a catalyst, a diamine component, and a dicarboxylic acid component, making them react and manufacturing nylon salt, it can manufacture easily by limiting viscosity's once considering as the prepolymer of 0.15 - 0.30 dl/g in the temperature of 280 degrees C or less, and carrying out solid state polymerization further, or performing a polymerization using a melting extruder. When solid state polymerization performs the culmination of a polymerization, if it is the range whose polymerization temperature is 200-250 degrees C, a rate of polymerization is large, and since it excels in productivity and coloring and gelation can be controlled effectively, it is desirable [ it is desirable to carry out to

the bottom of reduced pressure or inert gas circulation, and ]. When a melting extruder performs the culmination of a polymerization, since the polyamide which does not almost have decomposition of a polyamide as polymerization temperature is 370 degrees C or less, and does not have degradation is obtained, it is desirable.

[0019] As a polymerization catalyst, a phosphoric acid, phosphorous acid, hypophosphorous acid or those ammonium salt, those metal salts, and those ester can be mentioned, and sodium hypophosphite is desirable in respect of handling nature etc. in the ease of carrying out of acquisition especially. Moreover, stabilizers, such as a copper compound, a coloring agent, an ultraviolet ray absorbent, light stabilizer, an antioxidant, an antistatic agent, a flame retarder, a plasticizer, lubricant, a crystallization rate retarder, etc. can be added polycondensation reaction time or after that if needed. If alkali halide metallic compounds, such as halogenation copper compounds, such as organic system stabilizers, such as a hindered phenol, and copper iodide, and potassium iodide, are added especially as a thermostabilizer, since the melting stagnation stability in the case of fibrosis will improve, it is desirable.

[0020] Although melt spinning is carried out using a melting extruder and extension is usually given, as for the polyamide obtained as mentioned above, it is desirable to use a screw die pressing appearance machine. more than the melting point of a polyamide -- the temperature of 360 degrees C or less -- fusing -- the melting residence time for less than 30 minutes -- a mouthpiece -- it can fibrose by spinning from a nozzle. If melting temperature and the residence time are within the limits of the above, the pyrolysis of the polyamide at the time of spinning can be controlled.

[0021] Although it does not limit especially, when using it as a material of the separator for cells, it is [ that what is necessary is just to set up the fineness of this polyamide fiber suitably by various applications ] desirable that it is 0.1-5 deniers because of deposit prevention of the metal which constitutes the solution retention, positive electrode, and negative electrode of the electrolytic solution, and the short circuit prevention by migration of an electrode active material. In addition, a circular cross section or a variant cross section is sufficient as a fiber cross section, and, in the case of a variant cross section, let the value converted into the circular cross section be a diameter of fiber. Moreover, although especially fiber length is not limited, either, it can set up suitably by the formation approach of a nonwoven fabric. For example, it is desirable that it is 1-30mm when forming a nonwoven fabric with a wet method, and when forming a nonwoven fabric with dry process, such as the card method and the air lei method, it is desirable that it is 10-70mm.

[0022] The separator for cells of this invention consists of a nonwoven fabric which formed the above-mentioned polyamide fiber as a subject. As for a polyamide fiber, it is desirable that it is 50 % of the weight or more among a nonwoven fabric, and it is desirable that it is especially 70 % of the weight or more so that it may excel in the solution retention of the electrolytic solution.

[0023] In addition, the cellulosic fiber which mercerized the fiber; natural cellulose fiber of the compound gestalt which consists of polyolefine system resin independent, such as general-purpose aliphatic series polyamide; ethylene-vinyl alcohol system copolymers, such as nylon 6 and Nylon 66, polypropylene, polyethylene, polybutene, the poly methyl pentene, ethylene propylene rubber, and an ethylene-butene copolymer, or two kinds as fiber other than an above-mentioned polyamide fiber; the pulp by which marcerization was carried out can be mentioned. Moreover, the gestalt stability of a nonwoven fabric can also be raised by using fiber with the melting point lower than an above-mentioned polyamide fiber, well-known thermofusion nature binder fiber, a sizing agent, etc.

[0024] The nonwoven fabric concerning this invention can be obtained by the manufacture approach of arbitration. Fiber Webb (thing before interlacement of a nonwoven fabric or association) can be formed first, and it can manufacture with a general means to nonwoven-fabric-ize, by making the fiber in fiber Webb paste up or interlace. The obtained nonwoven fabric may be used as it is, and may be used as a layered product of two or more sheets. If there are wet methods, such as dry process, such as the card method and the air lei method, and a paper-making method, a span bond method, the melt blowing method, etc., for example, and fiber Webb obtained by the wet method or the melt blowing method also in these is precise, and it has a

uniform surface state as for Webb's formation approach and is used as a separator for cells, since a deposit of a metal and migration of an electrode active material can be prevented, it is suitable fiber Webb's formation approach. moreover, it can also be used combining fiber Webb formed by the approach of each above, carrying out a laminating.

[0025] An all directions method is explained concretely. Although formation of fiber Webb by dry process can manufacture fiber Webb using a roller card, Randa Muka-DO, a webber, etc. and this UEBBU is classified by parallel Webb, a clo sault ebb, a coulisse clo sault ebb, semi random Webb, and random Webb with the directivity of fiber, since the difference of a longitudinal direction and the direction of width on the strength becomes small, Webb of the configuration where the orientation approach of fiber crossed is suitable.

[0026] the approach of, for example, making fiber Webb interlacing according to an operation of a stream, a needle, etc. as an approach of forming a nonwoven fabric from such fiber Webb, the approach of making it paste with a binder, and sewing thread — a web — length — there is the approach of suturing reticulated etc., and these approaches are independent or can be combined.

[0027] Although formation of fiber Webb by the wet method has a common paper-making method, the approach of starting has a quick production rate compared with other approaches, and has the advantage which can mix the fiber from which the diameter of fiber differs with the same equipment, and the fiber of two or more classes at a rate of arbitration. That is, the gestalt of fiber also has the wide width of face of the shape of the shape of a staple, and pulp, etc. and selection, the application range is very wide and good Webb of formation who went that the diameter of use fiber was also usable to fiber thick from super-thin fiber is obtained. This approach is the approach of cutting first the fiber obtained by carrying out melt spinning, distributing underwater, considering as a uniform paper-making slurry also with that of churning gently, and carrying out paper making of this slurry for paper making using the paper machine which has at least one of the wires, such as a round mesh, a long network, and an inclination type. Moreover, a stream may be applied to independence or the sheet which carried out the laminating, and it may be made to interlace the wet paper web obtained by doing in this way, or the paper after desiccation. After beating processing is performed by the beater or the refiner, you may succeed in the cut fiber with a paper-making slurry, and it may add a \*\* agent, a dispersant, etc. in the case of paper making.

[0028] When forming the nonwoven fabric of 100% of polyamide fibers which contains neither adhesives nor other fiber substantially, the melt blowing method which blows off an elevated-temperature air current from a perimeter, \*\*-izes fiber, carrying out melt spinning, and accumulates this on an uptake side is suitable. Moreover, the span bond method which the \*\*-ized-extension-Webb formation process linked directly can also be used cooling the spun fiber, the extension approach is good also by the roller also in an air jet, and filamentation can be performed by the frictional electrification method, the compulsive charging method, the collision diffusion method, an air-current diffusion method, etc.

[0029] As for the front face of the nonwoven fabric formed by such approach, it is desirable to perform heat calendering for the manifestation of the improvement of surface smooth nature, thickness adjustment of a nonwoven fabric, reinforcement, and densification etc.

[0030] It is also possible to form a nonwoven fabric by Bath with the split film method or the foaming film method and the fiber method besides having mentioned above.

[0031] The separator for cells of this invention can be used as primary or a separator for rechargeable batteries. An open sand mold or closed mold is sufficient as this cell, and a cylindrical shape, a flat form, and a square shape are sufficient also as a configuration. It can more specifically be suitably used as a separator of rechargeable batteries, such as primary cells, such as an alkaline manganese dioxide cell, a mercury cell, a silver oxide cell, and an air cell, a nickel-cadmium battery, a silver-zinc cell, a silver-cadmium cell, a nickel-zinc cell, a nickel hydride battery, and a rechargeable lithium-ion battery. In addition, although this invention is a separator for cells, the nonwoven fabric concerning this invention is useful also as an air filter and a liquid filter.

[Translation done.]

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**EXAMPLE**

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[Example] Hereafter, although this invention is explained in full detail according to an example, this invention is not limited at all by these examples. In addition, each measured value in an example is a value measured by the following approaches.

(1) The basis weight of a nonwoven fabric (g/m<sup>2</sup>)

JIS P According to 8124, the nonwoven fabric was cut out on 10cm square, the weight W was measured with the electronic balance (the Metra Corp-company make, AE160 mold), and it computed by  $W/0.01$ .

(2) Powerful and breaking length of a nonwoven fabric (km)

JIS P the test piece which cut out the nonwoven fabric to 15mmx250mm according to 8113 — using — being powerful (kg / 15mm) — it measured and breaking length was computed.

(3) Air permeability (cc/m<sup>2</sup> / sec)

JIS L According to 1096, the nonwoven fabric was cut out on 20cm square, it considered as the test piece, and the air content which passes a test piece using the Flagyl mold testing machine was calculated.

[0033] (4) Alkali-proof JIS P According to 8113, immersion processing of the test piece of a nonwoven fabric was carried out for 60 hours into 70 degrees C and 10% of sodium-hydroxide water solution. The strength (kg / 15mm) of the test piece before and behind processing was measured, and it expressed with the retention on the strength.

(5) Anti-oxidation degradation nature JIS P It applies to 8113 correspondingly and is 5%KMnO<sub>4</sub> about the test piece of a nonwoven fabric. Immersion processing was carried out 30% for 1 hour at the mixed solution (the former/latter = 250/50 cc, 50 degrees C) of a potassium hydroxide. The strength (kg / 15mm) of the test piece before and behind processing was measured, and it expressed with the retention on the strength.

(6) Immersion processing of the test piece which cut the electrolytic-solution solution retention nonwoven fabric on 5cm square was carried out for 30 minutes at 20 degrees C and 30% of potassium hydroxide solution, and the liquid end by natural fall was performed in 30-second interspace mind. It is the weight of the test piece after W<sub>0</sub> and processing about the weight of the test piece before processing W<sub>1</sub> It carried out and the weight ratio ( $W_1 / W_0$ ) was computed as comprehensive liquid adsorption (g/g).

(7) Acid resistance JIS P According to 8113, immersion processing of the test piece of a nonwoven fabric was carried out for 100 hours into 70 degrees C and 10% of sulfuric-acid water solution. The strength (kg / 15mm) of the test piece before and behind processing was measured, and it expressed with the retention on the strength.

[0034] The terephthalic acid, 1, 9-nonane diamine, the 2-methyl -1, 8-octane diamine, the benzoic acid, the sodium hypophosphite-hydrate (it is 0.1 % of the weight to a raw material), and 2.2l. of distilled water of the amount shown in one to example of reference 7 table 1 were added to the autoclave of 20l. of content volume, and the nitrogen purge was performed. Subsequently, it agitated for 30 minutes at 100 degrees C, and the temperature up of the inside \*\* was carried out to 210 degrees C over 2 hours. At this time, the pressure up of the autoclave was carried out to 22kg/cm<sup>2</sup>. After continuing a reaction then for 1 hour, a temperature up is carried out to 230 degrees C, and it keeps at 230 degrees C after that for 2 hours, a steam is extracted



gradually, and it is a pressure of 22kg/cm<sup>2</sup>. The reaction was continued holding, next, 30 minutes — applying — a pressure — 10kg/cm<sup>2</sup> up to — the prepolymer was obtained for the reaction continuously [ it lowered and / for further 1 hour ]. Under 100 degrees C and reduced pressure, it dried for 12 hours and this prepolymer was ground to the magnitude of 2mm or less. The polymer was obtained by carrying out solid state polymerization of the grinding object under 230 degrees C and 0.1mmHg for 10 hours. The limiting viscosity of the obtained polymer is shown in Table 1.

[0035]

[Table 1]

		参考例 1 P A 9 T	参考例 2 P A 9 M T	参考例 3 P A 9 M T	参考例 4 P A 9 M T	参考例 5 P A 9 M T	参考例 6 P A 9 T	参考例 7 P A 9 M T
組 成	T A (モル)	19.4	19.7	19.5	19.5	19.6	20.0	20.2
	NMDA (モル)	20.0	17.0	14.0	10.0	10.0	20.0	17.0
	MODA (モル)	—	3.0	6.0	10.0	10.0	—	3.0
	安息香酸 (モル)	1.2	0.6	1.0	1.0	0.8	0.4	0.3
	NaH <sub>2</sub> P0 <sub>2</sub> H <sub>2</sub> O (モル)	0.06	0.06	0.06	0.06	0.06	0.06	0.06
極 限 粘 度		0.8	1.3	0.8	0.9	0.9	1.1	1.0
CONH/CH <sub>2</sub>		1/4.5	1/4.3	1/4.1	1/3.9	1/3.9	1/4.5	1/4.3

T A : テレフタル酸

NMDA : 1, 9 - ノナンジアミン

MODA : 2 - メチル - 1, 8 - オクタンジアミン

[0036] Melting extrusion of the polymer obtained in an example 1 — the examples 1-7 of 7 reference was carried out using the extruder, each rate was adjusted so that the ratio (draft) of discharge, a regurgitation rate, and a winding rate might become the range of 10-50 from the round hole nozzle of 0.2mm phix200 holes, and it rolled round in the 500-2000m range for /in winding rate. Subsequently, 85 degrees C and two baths performed extension / contraction processing using the water bath it is [ water bath ] 95 degrees C, and one bath obtained the tow of about 600 deniers / 200 filament. Draw magnification was performed by 0.8 times of the maximum draw magnification. 10% of the weight, it mixed 30% of the weight, and the synthetic pulp SWP (Mitsui petrochemical company make: E-400) which consists what cut the obtained tow in die length of 5mm of polyethylene 60% of the weight was used as the raw material for the thermofusion nature binder fiber (Daiwabo [ Co., Ltd. ] make: NBF-1) of polyethylene/polypropylene. Paper making of this raw material is carried out with a cylinder machine, and they are basis-weight about 70 g/m<sup>2</sup>. The nonwoven fabric was created. The heat press of this nonwoven fabric was carried out at 120 degrees C, and the separator for cells was obtained. These separators (nonwoven fabric) are evaluated and a result is shown in Table 2.

[0037] As example 8 polymer, it is a 2159.8 g (13. zero mol) terephthalic acid, The polymerization of the polymer (PA66IT is called) was carried out like the example 1 of reference except having used 830.2g (5.0 mols) of isophthalic acid, adipic acids 292.3g (2.0 mols) and 1, 2324.2 g (20. zero mol) 6-hexanediamine, a 24.43 g (0.2 mols) benzoic acid, 6.6g of sodium hypophosphite-hydrates, and 2.2l. of distilled water (limiting viscosity = 0.8, CONH/CH<sub>2</sub> = 1/3.6). The separator was created by the paper-making method like the example 1 using obtained PA66IT. This separator is evaluated and a result is shown in Table 2.

[0038] As example 9 polymer, it is a 1960.3 g (11. eight mols) terephthalic acid, isophthalic acid 1302. — the polymerization of the polymer (PA10IT is called) was carried out like the example 1 of reference except having used 5g (7.8 mols), 1, 3446.2 g (20. zero mol) 10-Deccan diamine, a 97.7 g (0.8 mols) benzoic acid, 6.2g of sodium hypophosphite-hydrates, and 6l. of distilled water (limiting viscosity = 0.8, CONH/CH<sub>2</sub> = 1/5). The separator was created by the paper-making method like the example 1 using obtained PA10IT. This separator is evaluated and a result is shown in Table 2.

[0039] The separator for cells was created by the paper-making method like the example 1

except having used the nylon 6 (Ube Industries [ Ltd. ] make: UBE Nylon 6) to which ring opening polymerization of the example of comparison 1 caprolactam was carried out. This separator is evaluated and a result is shown in Table 2. Although it excelled in alkali resistance and electrolytic-solution solution retention so that clearly from the result of Table 2, anti-oxidation degradation nature was low.

[0040] The separator for cells was created by the paper-making method like the example 1 except having used Nylon 66 (Ube Industries [ Ltd. ] make: UBE Nylon 66) which consists of example of comparison 2 hexamethylenediamine (aliphatic series diamine), and an adipic acid (aliphatic series dicarboxylic acid). This separator is evaluated and a result is shown in Table 2. Although it excelled in alkali resistance and electrolytic-solution solution retention so that clearly from the result of Table 2, anti-oxidation degradation nature was low.

[0041] The separator for cells was created by the paper-making method like the example 1 except having used the polyamide (Mitsubishi Gas Chemical [ Co., Inc. ] make: MX nylon 6007) which consists of example of comparison 3 meta-xylylene diamine (aromatic series diamine), and an adipic acid (aliphatic series dicarboxylic acid). This separator is evaluated and a result is shown in Table 2. Although it was thought because crystallinity is low that amide association was structurally weak since the polyamide consisted of aliphatic series JIKARUBON, in the anti-oxidation deterioration test, oxidation degradation was remarkably carried out in test fluid, and the configuration of a test piece did not remain.

[0042] 40% of the weight, it mixed 30% of the weight, the synthetic pulp SWP (Mitsui petrochemical company make: E-400) which consists of polyethylene the polyamide fiber (what was cut) by which spinning was carried out in the example of comparison 4 example 4 30% of the weight was used as the raw material for the thermofusion nature binder fiber (Daiwabo [ Co., Ltd. ] make: NBF) of polyethylene/polypropylene, and the battery separator was created by the paper-making method. This separator is evaluated and a result is shown in Table 2. Since there were few amounts of the polyamide fiber in a separator, electrolytic-solution solution retention was low.

[0043] The separator for cells was created by the paper-making method using example of comparison 5 polypropylene (Ube Industries [ Ltd. ] make: ZS1330). This separator is evaluated and a result is shown in Table 2. Although excelled in alkali resistance and anti-oxidation degradation nature, electrolytic-solution solution retention was low.

[0044]

[Table 2]

	材料種類	試験温度 ℃	評価結果						
			坪量 g/m <sup>2</sup>	強度 kg/15mm	裂断長 Km	透気度 cc/m <sup>2</sup> /sec	蓄水性 %	耐熱性 %	保液性 g/g
実施例 1	PA9T	340	69.9	0.61	0.58	18.4	99	97	2.61
" 2	PA9NT	330	70.0	0.71	0.68	16.4	95	93	2.76
" 3	PA9NT	330	72.3	0.70	0.65	17.1	94	94	2.59
" 4	PA9NT	310	71.1	0.80	0.75	17.8	96	96	2.64
" 5	PA9NT	310	70.8	0.68	0.64	18.1	97	94	2.80
" 6	PA9T	340	70.6	0.65	0.61	16.8	98	96	2.72
" 7	PA9NT	330	71.2	0.60	0.56	17.6	97	95	2.61
" 8	PA66IT	335	69.8	0.42	0.40	16.9	96	88	2.55
" 9	PA10IT	310	70.3	0.55	0.52	16.5	96	89	2.54
比較例 1	PA6	270	72.2	0.56	0.52	20.6	95	20	2.93
" 2	PA66	290	71.9	0.71	0.66	15.6	97	16	2.81
" 3	MXD	280	70.6	0.40	0.38	16.2	98	18	2.70
" 4	PA9NT	310	72.1	0.49	0.45	13.4	98	95	2.23
" 5	PP	220	71.1	0.71	0.67	10.1	100	100	2.09

[0045] The polymer obtained in an example 10 - the examples 1 and 4 of 11 reference was nonwoven-fabric-ized by the melt blowing method using the rectangle nozzle of 0.45mm phix300 holes. Manufacture conditions are shown in Table 3. Distance between a spinning nozzle and a

collector was performed by 100-300mm. The embossing calender-embossment set as 15% of sticking-by-pressure aspect products at the temperature which showed each nonwoven fabric in Table 3 performed embossing processing, and the separator was obtained. Each separator is evaluated and a result is shown in Table 3.

[0046] Nonwoven fabric-ization was performed by the melt blowing method like the example 9 using six to example of comparison 8 nylon 6, MX nylon, and polypropylene. Subsequently, embossing processing was performed and the separator was obtained. Each separator is evaluated and a result is shown in Table 3.

[0047]

[Table 3]

ポリマーの種類		実施例10	実施例11	比較例6	比較例7	比較例8
		PA9T	PA9MT	PA6	MXD	PP
製 造 条 件	ノズル温度(℃)	345	330	310	290	290
	空気温度(℃)	350	350	340	320	320
	空気圧力	2.8	2.7	2.5	2.3	2.1
	ホット温度(℃)	200	180	150	150	130
評 価	坪量 (g/m <sup>2</sup> )	73	74	69	72	71
	強力 (kg/15mm)	1.5	1.8	0.8	0.7	1.1
	裂断長 (mm)	1.37	1.62	0.78	0.65	1.03
	透気度(cc/m <sup>2</sup> /sec)	33.6	35.4	30.8	34.0	37.1
	耐アルカリ性(%)	98	99	95	98	100
	耐酸化劣化性(%)	99	98	0	0	100
	保液性(g/g) 総合	2.78	2.84	3.32	2.80	2.19
低	耐酸性 (%)	99	98	0	0	100

[Translation done.]